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PASSIVATION OF CREVICES

DURING ANODIC PROTECTION

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ABSTRACT

The protection of crevices poses an important problem in industrial applications of anodic protection. Experimental studies with a special crevice assembly have shown that the interiors of crevices often remain active and corrode at a rapid rate. These experiments, together with theoretical analyses, demonstrate that the ability to passivate crevices during anodic protection is controlled by electrolyte characteristics, crevice geometry, and the electrochemical behavior of the protected metal. Of these, critical anodic current density, i_c, is the most important parameter.

Anodic protection, first demonstrated by Edeleanu in 1954,[1] has been widely applied as an industrial corrosion control method.[2-5] Although the major advantages and limitations of this technique have been discussed in considerable detail,[6-8] the problems associated with the protection of crevices have been largely ignored. Crevice effects have probably not been troublesome in the past, since anodic protection has been generally restricted to storage tanks.[2-5] However, in more complex plant structures, crevices and other narrow electrolyte paths are invariably present. Examples include: threaded pipe sections, bolt and rivet holes and flanges. Also, unintentional crevices associated with porous welds and other surface defects are more likely in large systems.

In a previous study,[9] it was shown that a large potential gradient exists in crevices during potentiostatic anodic polarization. This gradient, caused by the high resistance of the narrow electrolyte path, often prevents the passivation of the crevice interior. Thus, although the exterior is maintained in the passive potential region, the interior remains active and rapidly corrodes.

The purpose of this investigation is to determine the factors influencing the anodic protection of crevices. This problem may be viewed as a special case of throwing power,[6,7,10] or the uniformity of current distribution.

EXPERIMENTAL

Most experiments were conducted with the special plexiglas electrode assembly illustrated in Figure 1. A cylindrical metal electrode, 2.65 inches in length, was press-fitted into the upper portion of the plastic mount, and attached to the external circuit by means of a Stern-Makrides Teflon gasket.[11] The electrode was centered in the precision-bored orifice with a measuring microscope ($\pm$ 0.0001 inch) to insure a uniform annular crevice opening of 0.009 inch. Geometrically, this assembly resembles a large bolted or riveted section.

The potential of the crevice exterior (bottom face of the cylindrical electrode) was measured with a glass Luggin-Haber probe, while the potentials within the crevice were determined by four internal Luggin-Haber probes at 0.5 inch intervals. Connection to these probes was achieved by a thistle tube-salt bridge sealed with a quartz wick. All potentials were measured relative to a saturated calomel electrode (S.C.E.).

Specimens of Type 304 and CF-8 stainless steel (Table I), water-quenched after 1 hour at 1095°C (2000°F), were used in these experiments. These were abraded on 2/0 emery paper, ultrasonically cleaned in detergent solution, rinsed in double-distilled water, and dried.

All tests were conducted in a multineck polarization cell containing hydrogen-saturated normal sulfuric acid at 25±°C. Solution level was maintained slightly above the uppermost probe opening. The potential of the crevice face was maintained constant within ± 1 mv. with an electronic potentiostat and the potentials of the crevice interior were determined. The polarization cell, auxiliary electrodes and related instrumentation have been described.[11-13]

In addition to the above experiments, potentiostatic anodic polarization measurements were performed in a conventional manner.[1,6,7,13] Specimens were preexposed for one hour, followed by 50 millivolt potential-step polarization at 5 minute intervals in hydrogen-saturated acid.

RESULTS

The potential distribution along CF-8 and Type 304 stainless steel crevices, 0.009 inch wide, as a function of external control potentials, are shown in Figures 2 and 3. These potential gradients are markedly different in spite of the similarities in crevice width and geometry. However, the respective anodic polarization curves show that the principal difference between these alloys is the value of critical anodic current density which is 2000 $\mu a/cm^2$ for the CF-8 and 76 $\mu a/cm^2$ for Type 304. Included in these Figures are current density distributions along the crevice at a 0.20 volt control potential. Such plots are constructed from the potential gradient and anodic polarization curve data.[7,10] Considering the 0.20 potential gradient of Figure 2, each crevice length defines a unique potential which has a corresponding current density value on the anodic polarization curve. For example, at 0.42 inch the crevice potential is -0.300 volt which corresponds to 2000 $\mu a/cm^2$ on the anodic polarization curve. Other points obtained in the same way define the complete current density distribution. At more noble control potentials the current density maximum moves to longer crevice lengths (e.g., 1.03 inch at 0.60 volts) and this shift increases the passive crevice length (Lp). It is evident in Figure 3 that the entire length of the Type 304 specimen is completely passive at a control potential of 0.20 volt.

The electrochemical data in Figures 2 and 3 are consistent with the appearances of specimens after extended testing. A specimen of CF-8 [illegible] hours at a control potential of 0.6 volt vs S.C.E. is shown in Figure 4. The unattacked or passive region is visible on the left, while the position of the current density maximum is indicated by the area of severe attack. Note that corrosion diminishes to the right of this point (slight grain faceting) as expected from the data in Figure 2.

Crevice width also has a pronounced influence, as shown in Figure 5. In this experiment, the potential at a depth of 0.25 inch was monitored at a constant external control potential of 0.20 volt. Crevices less than 0.0015 inch wide remain active (i.e., below 0.02 volt), while crevices wider than 0.002 inch are maintained passive to a depth of 0.25 inch.

DISCUSSION

The above results demonstrate that crevice potential is not an absolute value, but depends on crevice dimensions as well as anodic polarization characteristics. It is possible to relate these terms to the crevice length which can be passivated using the Fokin and Timonin analysis of potential distribution along thin wi es polarized in relatively large diameter tubes.[10]

During polarization, assuming the average current density under the polarization peak is 1/2 i_c, the total measured current, I, is:

$$I = 1/2\, i_c \pi d L_a + i_p \pi d L_p + i_p \pi d^2/4 \tag{1}$$

$$= 1/2\, i_c \pi d L_a \text{ for } i_c >> i_p \tag{1a}$$

where i_c = critical anodic current density
d = specimen diameter
L_a = active length
i_p = passive current density
L_p = passive length

From Ohm's Law and the resistivity equation these authors developed an equation for the passive length obtained by anodic protection. In terms of experimentally measurable values:

$$L_p = \frac{\Delta E_p \sqrt{D^2 - d^2}}{2\sqrt{i_c \Delta E_a \rho d}} \tag{2}$$

where D = orifice diameter= 0.387 inch = 0.984 cm for crevice assembly.
d = specimen diameter= 0.369 inch = 0.936 cm for crevice assembly
ρ = solution resistivity= 4.7 ohm-cm for $1\bar{N}(4.8\%)\ H_2SO_4$ at 25°C[14]
i_c = critical anodic current density
i_c(CF-8)= 2000 μ a/cm^2 and
i_c(304) = 76 μ a/cm^2
ΔE_p = passive potential range=$E_{control}$ - 0.02 volt*
ΔE_a = active potential range (defined by polarization peak)ΔE_a(CF-8)= 0.42 volt andΔE_a(304)= 0.36 volt

When D>>d this equation can be simplified and reduced

* The lower limit of the passive potential range is taken arbitrarily from anodic polarization data as 0.02 volt where the corrosion rate for both stainless steel alloys is 2 μ a/cm^2 ≅ 1 MPY.

to Edeleanu and Gibson's relation for wires polarized in tubes, which showed excellent correlation with experimental data.[7] However, the present work represents the first experimental test of the unmodified Equation 2, where $D \cong d$ for very narrow electrolyte paths.

Substituting the appropriate values for each alloy into the equation yields:

$$\text{for CF-8: } L_p(\text{cm}) = 2.42 \; \Delta E_p \qquad (3)$$

$$\text{for 304 : } L_p(\text{cm}) = 13.4 \; \Delta E_p \qquad (4)$$

In Table II, values of L_p calculated from these equations are compared with experimental measurements (i.e., crevice lengths at 0.02 volt) from Figures 2 and 3. The analysis yields excellent correlation for all values when portions of the crevice remain active at potentials below 0.02 volt.* However, when the entire crevice length becomes completely passive (i.e., L_p = L crevice) as in the case of Type 304 at control potentials above 0.10 volt, the Fokin-Timonin expression (Equation 2) is no longer applicable for analyzing the potential gradient curves, and another relationship must be developed to determine the crevice length which can be maintained passive.

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* These results are also in good agreement with the long term exposure test (Figure 4). The unattached region measures approximately 0.4 inch, which compares favorably with the experimental and calculated values of 0.50 and 0.55 inch, respectively.

The reason is evident from Equation 1a which becomes equal to zero when the active length $L_a=0$. For this situation, the second two terms of Equation 1 must be considered. For the crevice assembly $dL_p >> d^2/4$ and therefore the current for a completely passivated crevice is:

$$I = i_p \pi d L_p \tag{5}$$

Then, from Ohm's Law and the resistivity equation, the passive length maintained by anodic protection is determined:

$$L_p = 1/2 \sqrt{\frac{\Delta E_p \ (D^2-d^2)}{i_p d \rho}} \tag{6}$$

where $i_p = 2 \mu\ a/cm^2$ for Type 304 stainless steel.

The passive crevice length calculated from this equation for Type 304 alloy controlled at 0.20 volt shows good correspondence in Table II with the extrapolation of the experimental data to 0.02 volt. Comparison of these results with other data in the table clearly illustrates the extraordinary lengths which can be maintained passive once complete passivity is obtained. Similar observations have been noted in other anodic protection studies.[6, 7]

Methods for improving the feasibility of anodically protecting structures containing crevices follow directly from Equation 2. Since localized attack is avoidable only when the passive length equals or exceeds the crevice length, variables which increase the numerator and decrease the denominator of this equation are most advantageous. However, there are practical limitations which should be noted. The environment in industrial applications is generally fixed and therefore ρ is constant. Also, engineering designs, such as threaded sections or rivet construction, seldom can be widened to increase the $(D^2 - d^2)$ term. Obviously, any attempts to eliminate crevices with sealants or coatings must be complete, since very narrow crevices are the worst cases. In view of these restrictions, proper material selection is essential. Considering anodic polarization characteristics, the transpassive region (e.g., $E > 0.80v$ in Figure 2) where corrosion rate increases rapidly is the upper limit for control potentials. In a given environment, this potential is similar for most stainless steels, but may be considerably more noble or nonexistent for other materials such as titanium. The most important constant in Equations 3 and 4 is the critical anodic current density which can vary by orders of magnitude for different materials. In fact, other things being equal, a 10-fold decrease in i_c increases the passive length by a factor of 3.16. Thus, critical anodic current density is doubly important, since it also represents the magnitude of current necessary to achieve passivity during anodic protection.[1,6-8]

In determining the passive length from Equation 2 the most subtle restriction is the arbitrary definition of passivity involved in selecting the upper limit of ΔE_a. This potential range is similar for most stainless steels and provides only a minor contribution to the constants of Equations 3 and 4, but its interrelationship with ΔE_p does influence the magnitude of L_p. Choosing a smaller ΔE_a increment increases ΔE_p, thereby making the calculated and experimental passive lengths larger, although still in agreement. For example, in the 0.20 volt controlled potential experiment with Type 304, the passive crevice length calculated from Equation 4 is 0.95 inch. However, selecting ΔE_a=0.24 volt instead of 0.36 volt defines the lower passive potential limit at -0.10 volt, rather than 0.02 volt used in these experiments, and then L_p= 1.95 inch. Since the requirement for the complete passivity observed during this test is $L_p = L_{crevice} = 2$ inches, this greater L_p value is more nearly the actual passive length. However, this example illustrates the preference for overestimating ΔE_a, since a safety factor is provided in predicting the crevice length which can be passivated.

SUMMARY

1. The ability to passivate narrow crevices is an important factor in practical applications of anodic protection. In long, narrow crevices, internal portions of crevices often remain

active, resulting in rapid, localized corrosion.

2. Experiments with an anodically protected crevice assembly have shown that the Fokin-Timonin equation accurately predicts the length of the passive zone in partially protected, narrow crevices.
3. In selecting materials for anodic protection applications, it is important to choose alloys possessing small critical anodic current densities. This reduces the current requirements for initial passivation and improves the crevice-passivating ability of the system.

ACKNOWLEDGMENT

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TABLE I

ALLOY COMPOSITIONS

(Weight Percent)

CF-8		Type 304	
Cr	18.08	Cr	18.34
Ni	12.20	Ni	9.28
C	0.08	C	0.08
Mn	0.74	Mn	0.83
N	0.05	S	0.014
Si	1.22	Si	0.65
Fe	Balance	P	0.020
		Mo	0.11
		Cu	0.19
		Fe	Balance

TABLE II

Comparison of Calculated and Experimental

Protected Crevice Lengths

Alloy	$E_{control}$ (volts)	$\Delta E_p = E_{control} - 0.02$ (volts)	L_p (inches) Experimental	L_p(inches) Calculated)
	0.02	0	0	0.
	0.20	0.18	0.13	0.17
CF-8	0.40	0.38	0.27	0.36
	0.60	0.58	0.50	0.55
	0.80	0.78	0.81	0.74
	1.00	0.98	0.98	0.93
	0.02	0	0	0
304	0.10	0.08	0.37	0.42
	0.20	0.18	8.0*	8.3**

* Obtained by extrapolating potential gradient data to 0.02 volt.

** Calculated from Equation 6.

FIGURES

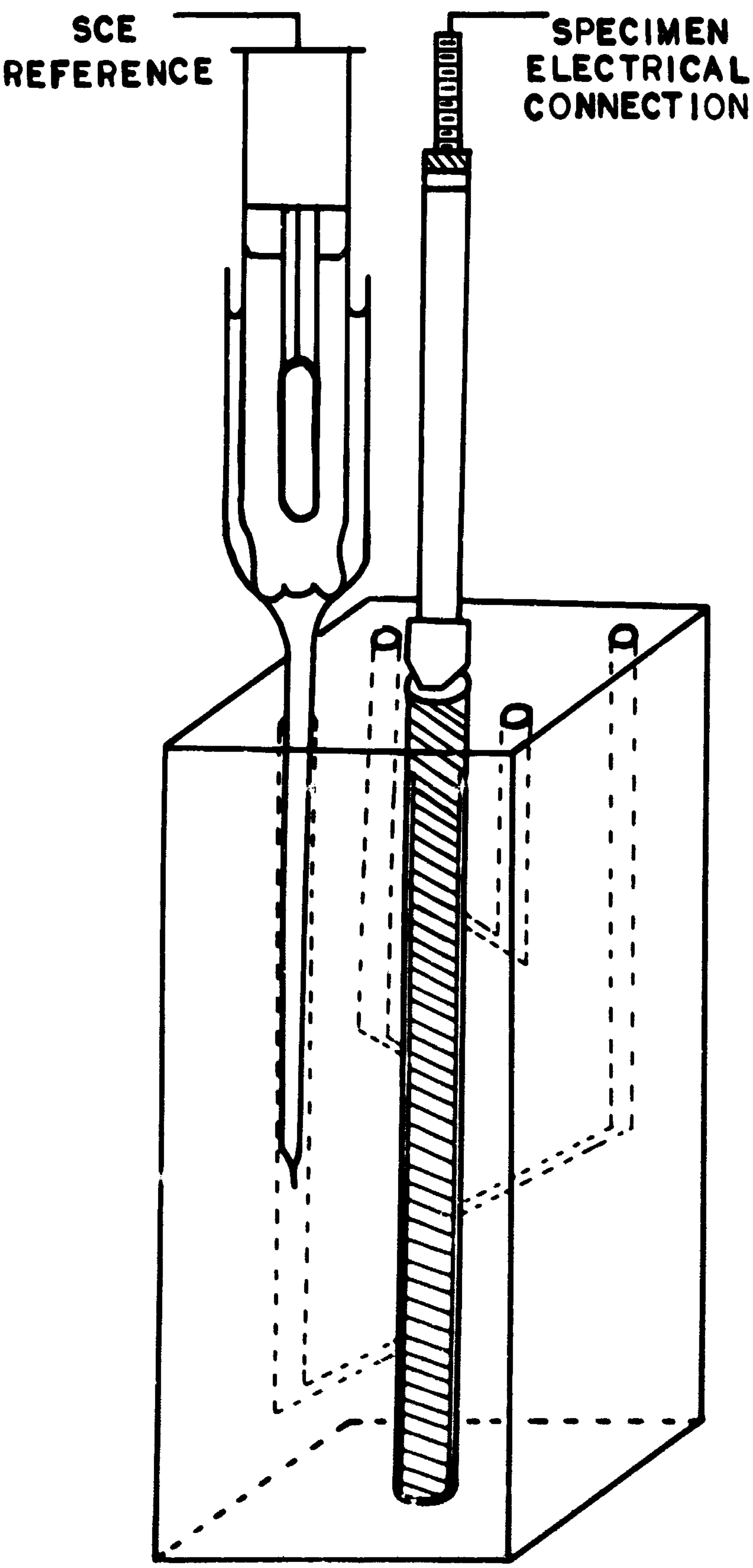
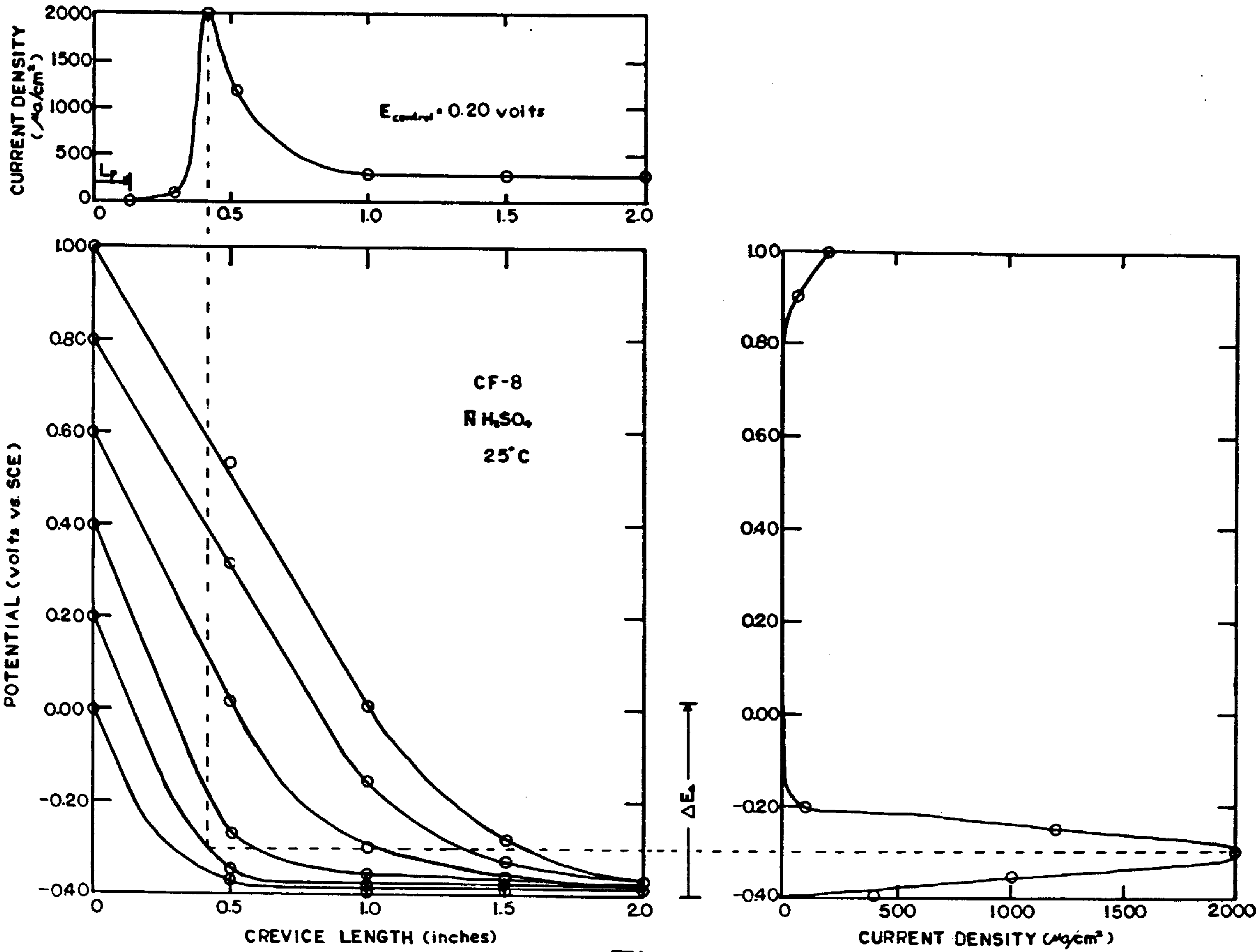
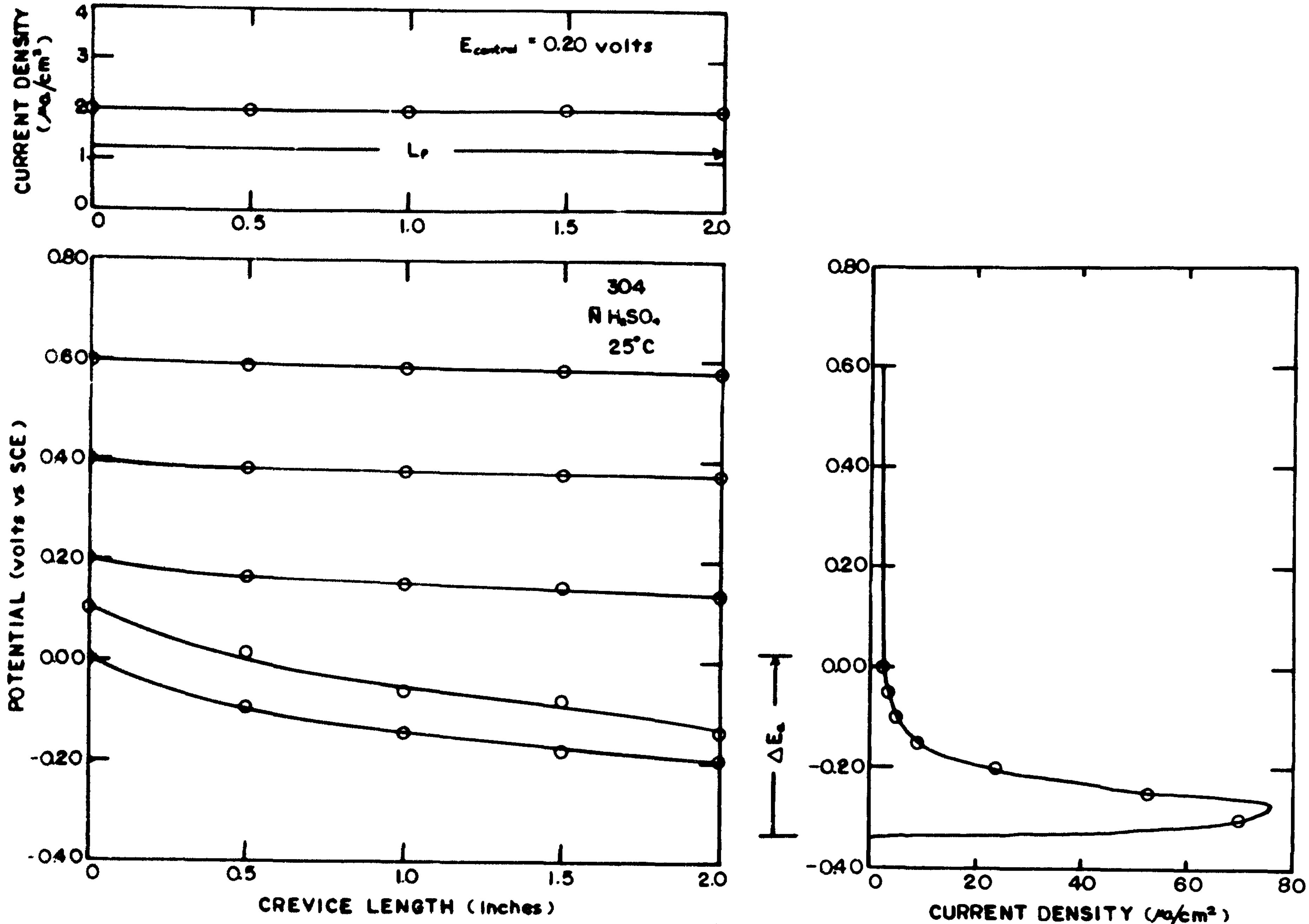


FIG.1



CURRENT DENSITY (μa/cm²)
2000
1500
1000
500
0
L_p
E control = 0.20 volts
0
0.5
1.0
1.5
2.0
POTENTIAL (volts vs. SCE)
1.00
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
CF-8
N H_2SO_4
25°C
CREVICE LENGTH (inches)
ΔE_p
CURRENT DENSITY (μa/cm²)

FIG.2



CURRENT DENSITY (μa/cm²)
E control = 0.20 volts
L_p
POTENTIAL (volts vs SCE)
304
N H₂SO₄
25°C
CREVICE LENGTH (inches)
ΔE
CURRENT DENSITY (μa/cm²)

FIG. 3

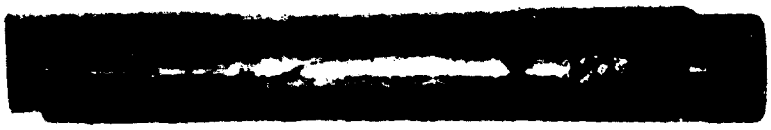
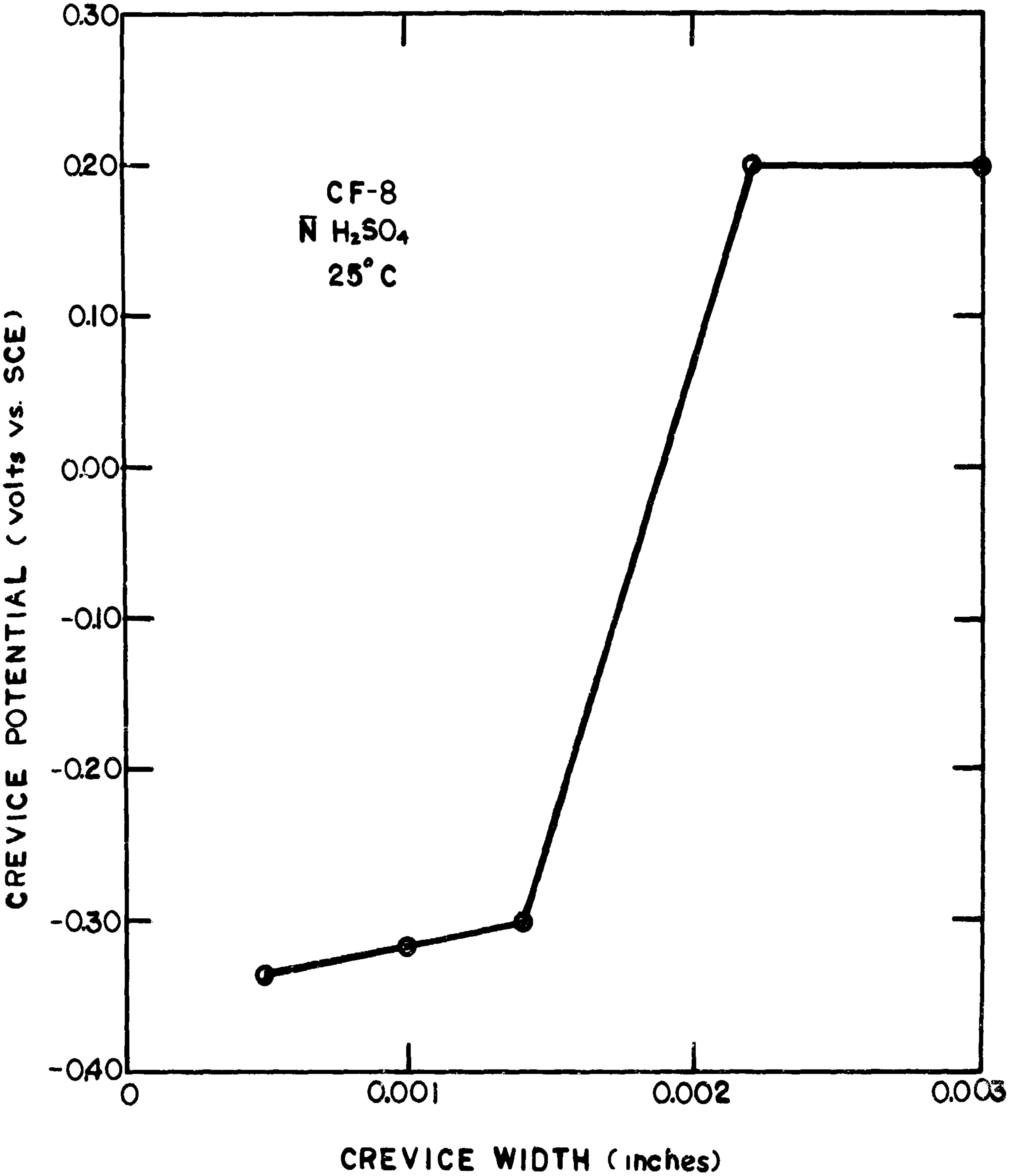


FIG. 4



CF-8
$\bar{N}$ H_2SO_4
25° C
CREVICE POTENTIAL (volts vs. SCE)
0.30
0.20
0.10
0.00
-0.10
-0.20
-0.30
-0.40
0
0.001
0.002
0.003
CREVICE WIDTH (inches)

FIG.5

Unclassified

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13. ABSTRACT

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Anodic Protection						
Potentiostatic Polarization						
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